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STUDY ON THE EFFECTS OF BLENDING *N*-BUTYL LEVULINATE WITH PALM METHYL ESTER ON THE FUEL PROPERTIES

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ABSTRACT

Alkyl levulinate can be synthesised from renewable levulinic acid and has the potential to be used as a fuel blend component. A variety of compounds can be blended with biodiesel to improve or attain the desired fuel properties. In this study, the effects of blending n*-butyl levulinate (BL) with palm methyl ester (PME) on fuel properties were evaluated. Blends of BL and PME (BL-PMEs) were prepared with 5%, 10% and 15% of BL. The addition of BL has improved the cloud and pour points by 7°C for 15BL-PME. As compared to ASTM D6751 and EN14214 specifications for biodiesel, BL-PMEs revealed properties within the specifications in terms of acid value, flash point, kinematic viscosity (40°C) and oxidative stability. The addition of BL up to 15% increased the acid value and decreased the flash point and kinematic viscosity. The oxidative stability increased slightly upon the addition of BL. The calorific value of BL-PMEs decreased with an increase in BL volume. Up to 10% BL, the calorific value is >35 MJ kg^{-1}. Besides, BL is highly miscible with PME and no phase separation was observed. The present work suggested that BL has potential as a bio-based fuel blend compound for biodiesel.*

Keywords: fuel properties, *n*-butyl levulinate, palm methyl ester.

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INTRODUCTION

Non-renewable energy generation has compelled the chemical industry to explore alternatives for energy and basic chemical production. Biomass has received significant attention for its potential as an alternative to fossil fuels. One of the promising biomass-derived chemicals is levulinic acid, which can be prepared from biomass through an acid hydrolysis process (Ramli and Amin, 2020). Levulinic acid possesses ketone carbonyl and acidic carboxyl groups which react differently to form a wide range of derivatives, thereby, making levulinic acid an ideal building block chemical.

Alkyl levulinate, or levulinate acid ester, is one of the levulinic acid derivatives, synthesised by direct esterification of levulinic acid with *n*-alcohol (Démolis *et al.*, 2014; Joshi *et al.*, 2011; Unlu *et al.*, 2018; Wang *et al.*, 2017). For instance, *n*-butyl levulinate can be produced from the esterification of levulinic acid with *n*-butanol. Both levulinic acid and *n*-butanol can be obtained from renewable feedstocks, making *n*-butyl levulinate bio-based chemicals. Alkyl levulinates can also be produced by direct conversion of biomass and cellulose; a major component of biomass. For example, the oil palm biomass, such as empty fruit bunch, trunks and oil palm fronds, contains a large amount of cellulose. With cellulose content of 45.2% and 38.2%, theoretical levulinic acid yields of 32.4% and 27.1% could be obtained from oil palm fronds and empty fruit bunch, respectively (Ramli and Amin, 2014). The levulinic acid can be further converted to alkyl levulinate. Alkyl levulinates have the potential to be applied in various areas including as a fuel blend compound, in fragrance and flavour, as a solvent and in the production of fine chemicals (Démolis *et al.*, 2014; Joshi *et al.*, 2011; Ramli and Amin, 2020; Unlu *et al.*, 2018; Wang *et al.*, 2017). Applications of alkyl levulinate have also been explored through their properties as pure fluid and in combination with other compounds (Ramli and Abdullah, 2021).

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Biodiesel or fatty acid methyl ester, derived from vegetable oil or animal fat, is a renewable fuel alternative to petroleum diesel fuel. Numerous researches have been conducted on biodiesel production from various feedstocks including palm oil. Comprehensive reviews on palm biodiesel / palm methyl ester (PME) and prospects for the economy, environment, suitability as a bioenergy crop, and its efficiency as a source of renewable fuel can be found in the literature (Mekhilef *et al.*, 2011; Parveez *et al.*, 2021). Some of the less favourable properties of biodiesel are its cold flow properties, such as high cloud and pour points, and low calorific value (Mekhilef *et al.*, 2011; Radhakrishnan *et al.*, 2017). The properties of biodiesel generally depend on the nature of its raw material as well as the technology or process used for its production. The biodiesel standards that are most referred to include European Standard for Biodiesel (EN 14214) and the American Standard Specifications for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels (ASTM D6751) (*Table 1*).

A variety of compounds and additives can be blended with biodiesel to enhance or attain the desired properties (Ali *et al.*, 2014; Cao *et al.*, 2014; Rashedul *et al.*, 2014). Over the years, research has been conducted to produce sustainable and bio-based fuel blend compounds and additives, and investigate their effect on biodiesel properties. As reviewed elsewhere, the compounds can be classified in terms of their point of application such as oxygenated compound, cold flow improver, and cetane number improver (Rashedul *et al.*, 2014). The use of oxygenated compound additives for example alcohol (methanol, butanol, propanol, *etc.*), ether (diethyl ether, diisopropyl ether, *etc.*), and ester (dicarboxylic acid esters and acetoacetic esters) functional groups, is to enhance the combustion quality. The commonly use cold flow improver is vinyl ester co-polymer such as ethylene vinyl acetate, while the cetane number improver includes alkyl nitrates (2-ethyl hexyl nitrate) and peroxides (tertiary butyl peroxide) (Rashedul *et al.*, 2014).

Similar to the oxygenated compounds that are generally used as biodiesel blend components and additives such as alcohol, ether, and ester functional group, alkyl levulinate is also regarded as an oxygenated compound (Christensen *et al.*, 2011b; Rashedul *et al.*, 2014). Several studies have reported the potential of ethyl levulinate to be used as a blend component for biodiesels such as cottonseed oil, poultry fat, canola oil and dairy-washed milk scum biodiesels (Joshi *et al.*, 2011; Srikanth *et al.*, 2017; Unlu *et al.*, 2018). Based on the findings from a previous study, *n*-butyl levulinate (BL) is miscible with diesel when compared to ethyl levulinate with poor solubility thus making the use of ethyl levulinate as a diesel blend component technically challenging (Christensen *et al.*, 2011a). Due to the miscibility factor, BL has been applied as a blend component in fuels containing diesel, gasoline and biodiesel-diesel-butanol-ethanol (Christensen *et al.*, 2011a; 2011b; Hashim *et al.*, 2017). In contrast to the alkyl levulinate with shorter carbon chain lengths such as methyl and ethyl levulinate, *n*-butyl levulinate is expected to have better fuel properties such as higher calorific value and improved low-temperature performance; cloud and pour point. This is supported by the findings of the considerable improvement in low-temperature properties from methyl to butyl for octadecenoic esters, which is explained by the interactions established between the esters (Wang *et al.*, 2020). Nevertheless, no study has been reported about the effect of BL on the neat PME in terms of fuel properties.

Therefore, in the current study, BL is selected for further testing as PME blends. The effect of blending BL with PME on the fuel properties was evaluated. Blends of BL-PMEs were prepared with 5%, 10% and 15% of BL. The effect of BL on acid value, cloud point, pour point, flash point, kinematic viscosity, oxidative stability, and calorific value was determined accordingly. The fuel properties of BL-PMEs were compared with specifications for biodiesel by ASTM D6751 and EN 14214.

TABLE 1. SELECTED SPECIFICATIONS FOR BIODIESEL (ASTM D6751 AND EN 14214)

Property	ASTM D6751		EN 14214	
	Specification[a]	Method	Specification[a]	Method
Flash point, °C	Min. 93	ASTM D93	Min. 101	EN ISO 2719
Kinematic viscosity (40°C), $mm^2\ s^{-1}$	1.9–6.0	ASTM D445	3.5–5.0	EN ISO 3104
Density (15°C), $kg\ m^{-3}$	-	-	869–900	EN ISO 3675
Cloud point, °C	Report	ASTM D2500	-	EN 23015
Acid value, mg KOH g^{-1}	Max. 0.50	ASTM D664	Max. 0.50	EN 14104
Oxidative stability, hr	Min. 3	EN 14112	Min. 6	EN 14112
Cetane number	Min. 47	ASTM D613	Min. 51	EN ISO 5165

Note: [a] Max. is the maximum value, Min. is the minimum value.

MATERIALS AND METHODS

Materials

Palm methyl ester (PME) or palm-based biodiesel was obtained from Sime Darby Oils, Malaysia. The selected properties of PME are reported in *Table 2*. The commercially available *n*-butyl levulinate (BL) was purchased from Sigma Aldrich, CAS 2052-15-5. The purity of BL (99.4%) has been verified using a gas chromatography-flame ionisation detector (GC-FID) (Ramli and Abdullah, 2021). The materials were of sufficient purity and were used as received without further purification.

TABLE 2. PROPERTIES OF PALM METHYL ESTER (PME)

Parameters	Method	Specification[a]	Value
Water content, mg kg^{-1}	EN ISO 12937	500 max.	257
Acid value, mg KOH g^{-1}	EN 14104	0.50 max.	0.24
Iodine value, g iodine 100 g^{-1}	EN 14111	110 max.	52.68
Ester content, %	EN 14103	96.5 min.	99.89
Density (15°C), kg m^{-3}	EN ISO 12185	860–900	875.2
Flashpoint, °C	EN ISO 2719	120 min.	172
Oxidative stability, hr	EN 14112	10 min.	>15

Note: [a] Max. is the maximum value, Min. is the minimum value.

Methods

Fatty acid profile of PME. The fatty acid methyl esters (FAME) were separated using GC-FID (6890 Agilent) equipped with a capillary column HP-88 (60 m × 250 µm × 0.2 µm). The carrier gas was He at 0.8 mL min^{-1}. The oven temperature was initially held at 150°C, and then programmed to 210°C for 10 min at a rate of 3°C min^{-1}. The injector and detector temperatures were both set at 250°C. The FAME peaks were identified by comparison to known reference standards. Analysis was run in duplicate and mean values were reported.

Preparation of BL-PME blends. Three BL-PME blends were prepared prior to analysis of their properties. The measured quantity of BL was added to PME with constant stirring using a magnetic stirrer for proper mixing. PME was blended with 5%, 10% and 15% of BL. These BL-PMEs were denoted as 5 BL-PME, 10 BL-PME and 15 BL-PME, respectively. Pure samples of BL and PME were kept for control purposes.

Determination of BL, PME and BL-PMEs fuel properties. The properties of BL, PME and BL-PMEs were determined according to standard methods. All analyses were made in duplicate for each sample and the mean value was recorded.

The acid value was determined based on the titration method (mg KOH g^{-1}) according to AOCS Cd 3d-63. The described method is by visual indicator using phenolphthalein, which is similar to EN 14014. The sample was weighed into a conical flask, and 125 mL of the neutralised isopropanol was added, followed by a few drops of phenolphthalein. Complete dissolution of the sample was ensured before titration. The flask was gently swirled while titrated with potassium hydroxide (KOH) standard solution until the appearance of the first permanent pink colour. The acid value was calculated as in Equation (1).

$$\text{Acid value (\%)} = \frac{56.1 \times \mathrm{M} \times \mathrm{V}}{\mathrm{m}} \qquad (1)$$

where M is the molarity (M) of KOH solution, V is the volume (mL) of KOH solution and m is the mass (g) of the sample.

Cloud point was determined in accordance with ASTM D2500, using CPP Classic from Normalab (Belgium) to an accuracy of ± 1°C. The sample (50 mL) was cooled in a test jar and was observed at intervals of 1°C decrement. The temperature at which a cloudy structure became visible was noted as the cloud point. The cloud point value was rounded to the nearest whole value (°C).

The pour point was determined in accordance with ASTM D97. Pour point was measured using CPP Classic from Normalab (Belgium) to an accuracy of ±1°C, by placing a test jar containing 50 mL of sample into a cylinder submerged in ethanol (95%) as the cooling medium. The test jar was held in a horizontal position for 5 s at every 3°C decrements and stopped when the sample was no longer flowing within 5 s in a horizontal position. The pour point was taken as 3°C above the temperature at which the sample was no longer flowing. The pour point value was rounded to the nearest whole value (°C).

Flashpoint was determined using Pensky-Martens closed cup method, ASTM D93. The measurement was performed using PMA 5 Automatic Pensky Martens closed-cup flash point tester – Procedure A. The closed-cup tester measures the flash point at the lowest temperature at which the application of an ignition source causes the vapours of a sample to ignite. A test cup is filled with the sample and the lid is then placed on the test cup. Based on the program selected, the sample is heated at 5°C-6°C min^{-1} and stirred at specified rates of 90-120 rpm, and then the ignition source is directed into the test cup.

Kinematic viscosity was obtained using ASTM D445. The test method measures the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The measurement was carried out using PMT Tamson NVB Classic (Normalab, France) with a viscometer bath set at 40°C and 100°C. The capillary viscometers and the constant temperature bath were purchased from Cannon Instruments, State College, PA.

The oxidative stability test was performed according to Rancimat method EN 14112 using 743 Rancimat Apparatus (Metrohm, Switzerland). The Rancimat method is an accelerated oxidation test that is run at elevated temperatures and exposes the sample to air. Three grams of sample were heated to 120°C with an airflow rate of 20 L hr^{-1}. The time taken up to the inflection point of conductivity versus the time curve was determined based on the conductimetric method.

The calorific value was determined using a bomb calorimeter Parr 6100 according to ASTM D240. The standardisation of the calorimeter was performed using benzoic acid. The sample was burned in the presence of oxygen inside a sealed container. The heat released from combustion is transferred to a mass of water that surrounds the container. The calorific value represents the gross heat of combustion of the sample.

Data analysis. Data obtained were subjected to analysis of variance (ANOVA) in the IBM SPSS Statistics (Version 23.0). Linear contrasts were used to determine the effects of BL contents on fuel properties using α=0.05. The linear contrast examines whether the BL-PME was significantly different from the control (PME), and whether varying the BL content had a significant effect on the properties. The significance level was accepted at $p \leq 0.05$.

RESULTS AND DISCUSSION

Fatty Acid Composition of PME

The analysis of fatty acid profiles shows that palm methyl ester (PME) contained fatty acids as in *Table 3*. It is reported that biodiesel which contains high saturated fatty acid or low unsaturated fatty acid results in poor cold flow properties; cloud, pour and cold filter plugging point (Lv *et al*., 2013; Unlu *et al*., 2018; Verma *et al*., 2016). In addition, the presence of high unsaturated fatty acid esters makes it prone to autoxidation, which could reduce the oxidation stability. As in the current study, the fatty acid profiles of PME revealed an equal proportion of saturated (49.6%) and unsaturated (50.3%) fatty acids.

TABLE 3. FATTY ACID COMPOSITIONS OF PALM METHYL ESTER (PME)

Fatty acid	Composition (%)
Lauric (C12:0)	0.2
Myristic (C14:0)	1.1
Palmitic (C16:0)	43.5
Palmitioleic (C16:1)	0.2
Margaric (C17:0)	0.1
Stearic (C18:0)	4.3
Oleic (C18:1)	39.8
Linoleic (C18:2)	10.0
Linolenic (C18:3)	0.2
Arachidic (C20:0)	0.4
Eicosenoic (C20:1)	0.1
Others	0.1

Fuel Properties of BL, PME and BL-PMEs

Miscibility is the basic requirement of fuel blends for storage, transportation and utilisation (Wang *et al*., 2017). In this study, it is implied that *n*-butyl levulinate (BL) is highly miscible with PME. From the visual inspection, no phase separation was observed when blending BL with PME for all fuel blends for more than 72 hr at 25°C-30°C. All samples were stirred well prior to the analysis of each test to ensure the miscibility and homogeneity of BL-PMEs.

As given in *Table 4*, the properties of the control sample PME are within the specified limits by ASTM D6751 and EN 14214 (*Table 1*) for acid value, flash point, kinematic viscosity and oxidative stability. Meanwhile, the properties of BL are within the specifications in terms of acid value, flash point and oxidative stability. The kinematic viscosity of BL did not meet the requirement of EN 14214 but is within the specification of ASTM D6751. The trends and effects of BL addition on BL-PMEs properties are given in the following section.

Effects of BL on Acid Value of BL-PME

Biodiesel composes of fatty acid methyl esters and also small amounts of fatty acids, which are quantified by an acid number, expressed as milligrams of potassium hydroxide required to neutralise 1 g of sample (mg KOH g^{-1}). The high acid value of fuel results in the accumulation of solid particles in the fuel system, which could cause problems in the filters and pumps, and can cause motor corrosion (Unlu *et al*., 2018).

In this study, the acid value of BL and PME, 0.47 and 0.27 mg KOH g^{-1}, respectively, are within the ASTM D6751 and EN 14214 requirements. As reported in the literatures, the acid value of BL was 0.40 (Christensen *et al*., 2011a), while the acid value of other alkyl levulinates; ethyl levulinate was 0.16 mg KOH g^{-1} (Lei *et al*., 2016), 0.36 mg KOH g^{-1} (Joshi *et al*., 2011) and 0.70 mg KOH g^{-1} (Christensen *et al*., 2011a). It is presumed that the different

TABLE 4. FUEL PROPERTIES OF BL, PME AND BL-PMES

Vol% BL[a]	Properties[b]						
	AV, mg KOH g^{-1}	CP, °C	PP, °C	FP, °C	KV, mm^2 s^{-1}	OS, hr	CV, MJ kg^{-1}
BL blended with PME[a]							
0	0.27	15	12	174	4.496	13.7	40.3
5	0.28	11	10	159	4.325	14.3	38.7
10	0.31	10	7	151	4.088	14.5	35.1
15	0.33	8	5	143	3.908	14.6	31.4
Control sample[a]							
BL	0.47	<-42	<-42	111	1.997	28.0	27.9
PME	0.27	15	12	174	4.496	13.7	40.3
Contrast[c]							
1[d]	0.011	0.002	0.004	<0.001	0.009	0.001	<0.001
2[e]	0.008	0.047	0.005	<0.001	0.014	0.008	<0.001

Note: [a]BL-*n*-butyl levulinate; PME-palm methyl ester; BL-PMEs-blends of *n*-butyl levulinate with PME; [b]AV-acid value; CP-cloud point; PP-pour point; FP-flash point; KV-kinematic viscosity at 40°C; OS-oxidative stability; CV-calorific value; [c]*p*-value at α=0.05; [d]Whether BL-PME was significantly different from control sample, PME, [e]Whether varying BL from 5% to 15% had significant effect on fuel properties.

acid value reported for alkyl levulinate is due to the residual levulinic acid, as alkyl levulinate is generally prepared from the esterification of levulinic acid (Christensen *et al.*, 2011a). As in this study, BL has been stored prior to testing. This condition may cause oxidation and hydrolysis which resulted in increased acid value (Christensen *et al.*, 2011a). Therefore, the difference in the acid value of BL from this study and literature is possibly due to the partial hydrolysis that occurred during the shelf storage.

The acid value of BL-PMEs was significantly different from PME (*p*<0.05) and increased visibly as the BL increased from 0% to 15% (*Table 4*). Nevertheless, the maximum addition of 15% BL was found to be within ASTM D6751 and EN 14214. A previous study also reported the increase in acid value on the addition of ethyl levulinate up to 20% in canola oil biodiesel, where a maximum addition of 10% ethyl levulinate was found a suitable amount according to standards for the acid number (Unlu *et al.*, 2018). The increasing trend of acid values may limit the application of the blend component on biodiesel with high acid values (Lawan *et al.*, 2019). However, there is no clear trend in the acid value from the application of ethyl levulinate as a blend component (0%-20%) to cottonseed oil and poultry fat biodiesels (Joshi *et al.*, 2011).

On the other hand, several studies revealed that the addition of a fuel blend component improved the acid value of biodiesel. For example, reduction of acid value by increasing the blend components; ethanol, isopropanol and butanol up to 20% in poultry fat biodiesel (Joshi *et al.*, 2010), 20% of ethyl acetoacetate in waste cooking oil biodiesel (Cao *et al.*, 2014), 20% of ethyl acetoacetate and ethyl levulinate in dairy washed milk-scum biodiesel (Srikanth *et al.*, 2017), and 7% of 1-butanol in palm biodiesel (Ali *et al.*, 2014). It is suggested that the reduction in acid value is because the blend components diluted the free fatty acids present in the biodiesel (Ali *et al.*, 2014; Joshi *et al.*, 2010). From these studies, all blends exhibited acid values that were satisfactory compared to ASTM D6751 and EN 14214.

Effects of BL on Cloud Point and Pour Point of BL-PME

Cloud points and pour points are usually used to assess the cold flow properties of fuels. A cloud point indicates the temperature at which a cloud of wax crystals first appears in a clear liquid product when the liquid is cooled under specified conditions (Hui *et al.*, 2009). The addition of BL to PME generally resulted in lower cloud points (*Table 4*). The BL-PMEs showed a pronounced decrease in cloud point as the BL concentration increased (*p*<0.05). The BL-PMEs portrayed cloud point reduction of 7°C at 15BL-PME. This may be attributed to the low melting point of BL (<-60°C) (Christensen *et al.*, 2011a), which is much lower compared to the cloud point of PME (15°C).

ASTM D6751 requires cloud point to be reported, while there is no such requirement for cloud point in EN 14214. A similar trend of decreasing cloud points as the blend component's concentration increases has also been reported in various studies. For example, reduction of 15°C for ethyl levulinate-canola oil biodiesel (Unlu *et al.*, 2018), 14°C for ethanol-palm biodiesel (Verma *et al.*, 2016), 9°C for ethyl levulinate- and ethyl acetoacetate-dairy washed milk scum biodiesel (Srikanth *et al.*, 2017), 6°C-7°C for alcohol (ethanol, isobutanol, propanol), poultry fat biodiesel (Joshi *et al.*, 2010), 4°C for ethyl levulinate-cottonseed oil biodiesel and ethyl acetoacetate-waste cooking oil biodiesel (Cao *et al.*, 2014; Joshi *et al.*, 2011), and 5°C for ethyl levulinate-poultry fat biodiesel (Joshi *et al.*, 2011). The saturated esters are prone to precipitate as the temperature is lowered (Joshi *et al.*, 2011; Srikanth *et al.*, 2017). The decreasing of cloud point with increasing concentration of the blend component is possibly due to the blend component acting as a diluent, which prevented the coagulation of the esters at low temperatures (Cao *et al.*, 2014; Joshi *et al.*, 2011; Srikanth *et al.*, 2017).

As the temperature drops, fuel tends to get solidified until it achieves its pour point; the lowest temperature at which the fuel can flow (Verma *et al.*, 2016). The pour point is not required in ASTM D6751 and EN 14214, but it provides additional information about the cold flow properties of the fuel. It indicates the temperature at which the sample can be cooled without losing its fluidity. The effect on pour point from the addition of BL to PME was similar to the trend elucidated for cloud point. The pour point decreased significantly ($p<0.05$) with an increasing amount of BL (*Table 4*). The pour point of BL-PMEs decreased by 7°C with an increasing amount of BL added up to 15%. Overall, the trend suggested that the cold flow properties; cloud and pour point of BL contributed to the improvement of the cold flow properties of BL-PME.

A similar trend for cloud and pour points was also reported in the previous studies. The significant reduction of pour points is due to the low freezing temperature of the blend component, which is substantially below the temperature at which biodiesel typically undergoes solidification (Ali *et al.*, 2014). For instance, the freezing point of 1-butanol is -90°C, resulting in the decrease of the pour point from 16°C to 9°C by increasing the 1-butanol content up to 7% (Ali *et al.*, 2014). Besides, ethyl levulinate with a freezing point <-79°C resulted in a reduction of pour point by 3°C to 6°C (Joshi *et al.*, 2011; Srikanth *et al.*, 2017). It is proposed that the application of the blend compounds and the appropriate blending amount should be evaluated based on the application conditions. This is because, neither the ASTM D6751 nor EN 14214 specification state the maximum or minimum requirements of fuel temperature properties, including cloud and pour point, since it is the location and seasonal dependant.

Effects of BL on Flash Point of BL-PME

The flash point of a fuel is defined as the minimum ignition temperature at which fuel produces enough vapour to cause ignition leading to flame generation (Arbab *et al.*, 2013). The flash point is related to the safety requirements for handling and storage of fuel (Kaisan *et al.*, 2020). Higher flash point makes fuel safer for handling and storage and could prevent unexpected ignition during combustion. Most biodiesels possess higher flash points than that diesel (Arbab *et al.*, 2013). For a compound with a very low flash point, its use as a standalone fuel blend component could potentially deteriorate the safe storage criterion of the fuel (Mohammadi *et al.*, 2014).

Varying the BL content from 5% to 15%, the flash point decreased significantly ($p<0.001$), which is due to the lower flash point of BL. Nevertheless, the flash point of 5-, 10- and 15BL-PME are all still within the specifications of ASTM D6751; minimum of 93°C, and EN 14214; minimum of 101°C. The findings from previous studies also reported a similar trend. In previous studies on the effect of ethyl levulinate and ethyl acetoacetate as a blend component to cottonseed oil, poultry fat, dairy-washed milk scum and waste cooking oil biodiesels, the flash point for all samples were above the ASTM D6751 limit, but the 20% blends reported flash point below 101°C (Cao *et al.*, 2014; Joshi *et al.*, 2011; Srikanth *et al.*, 2017).

Furthermore, a significant reduction in flash points was observed as alcohols (ethanol, isopropanol and butanol) were blended with biodiesel (Cao *et al.*, 2014; Joshi *et al.*, 2011; Srikanth *et al.*, 2017). This is due to the low flash point of the respective alcohols. Nevertheless, a further increase of the alcohol content from 5% to 20% has minimal effect on the flash point (Joshi *et al.*, 2010). In terms of alcohol, biodiesel blended with longer carbon chain alcohol gives better flash points, which is due to their higher flash point. For example, the flash point for 50% of pentanol blended with *Calophyllum inophyllum* biodiesel is within ASTM D6751 specification, while 50% of butanol blend did not meet the specification (Nanthagopal *et al.*, 2018). Even though the flash points of biodiesel due to the addition of fuel blend component were within the limits suggested by ASTM D6751 and EN 14214, the variations in the flash points could limit the utilisation of the respective blend component on other biodiesels with relatively lower flash points (Lawan *et al.*, 2019).

Effects of BL on Kinematic Viscosity of BL-PME

Biodiesel has a higher viscosity than petroleum diesel as reflected in the relevant standards, which are 1.9–6.0 $mm^2\ s^{-1}$ and 3.5–5.0 $mm^2\ s^{-1}$ according to ASTM D6751 and EN 14214, respectively, for biodiesel, and 1.9–4.1 $mm^2\ s^{-1}$ according to EN 590 for petroleum diesel (Smith *et al.*, 2010). Fuels with high kinematic viscosity increase fuel consumption and cause poor fuel spray and atomisation (Arbab *et al.*, 2013). In terms of combustion and emission, fuel with lower kinematic viscosity enhances the contact between air and fuel during combustion and lower NOx emissions (Radhakrishnan *et al.*, 2017). Nevertheless, fuel with both low and high viscosities, which exceeds the upper and lower limit of the specification, can hurt fuel performance. For example, fuel with low viscosity does not provide sufficient lubrication (Isioma *et al.*, 2013).

In contrast to PME, the kinematic viscosity of BL-PME was significantly different ($p<0.05$) (*Table 4*). As the percentage of BL increased, a decrease in kinematic viscosity was observed ($p<0.05$), which is due to the lower kinematic viscosity of BL than that of PME. In previous studies, with considerably lower kinematic viscosities for ethyl levulinate (1.50 $mm^2 s^{-1}$) and ethyl acetoacetate (1.63 $mm^2 s^{-1}$) compared to biodiesel, the kinematic viscosity of fuels containing these compounds did not meet the EN 14214. For instance, 20% of ethyl levulinate in cottonseed oil, poultry fat and canola oil biodiesels (Joshi *et al.*, 2011; Unlu *et al.*, 2018), 15% of ethyl levulinate and ethyl acetoacetate in dairy-washed milk scum biodiesel (Srikanth *et al.*, 2017), and 20% of ethyl acetoacetate in waste cooking oil biodiesel (Cao *et al.*, 2014). Meanwhile, as butanol and pentanol possess higher kinematic viscosity (2.6-2.9 $mm^2 s^{-1}$), the addition of these compounds to *C. inophyllum* and palm biodiesels also caused lower kinematic viscosity of the fuel blends (Nanthagopal *et al.*, 2018; Radhakrishnan *et al.*, 2017). Nevertheless, the kinematic viscosities are within ASTM D6751 and EN 14214 for butanol and pentanol addition up to 60% (Nanthagopal *et al.*, 2018).

Effects of BL on Oxidative Stability of BL-PME

Oxidative stability affects the stability of biodiesel during extended storage. Biodiesel with a higher percentage of saturated fatty acid possesses higher oxidation stability (Srikanth *et al.*, 2017). The requirement of oxidative stability for biodiesel is a minimum of 3 and 6 hr for ASTM D6751 and EN 14214, respectively. Meanwhile, a more stringent limit was set by the Malaysian Standard for PME, MS 2008, which is 10 hr minimum. The use of antioxidants; natural and synthetic, is effective to tackle the oxidative stability challenges for biodiesel (Lawan *et al.*, 2019). Antioxidants are components which prevent auto-oxidation of oils and fats by giving their hydrogen to free radicals formed in the initiation and propagation stages of autoxidation (Lawan *et al.*, 2019).

In the current study, the initial oxidative stability of the PME sample was 30.4 hr (*Table 2*). The PME has been stored after the procurement and before the preparation of BL-PMEs and the determination of oxidative stability. The decrease in oxidative stability of PME is due to the prolonged storage period. During the time of analysis, the oxidative stability of control samples BL and PME are 28.0 and 13.7 hr, respectively. The increase in BL from 5% to 15% increased the oxidative stability of BL-PME ($p<0.05$) from 14.3 to 14.6 hr. Even though the oxidative stability of BL is higher compared to PME with a difference of 1.04 times, the addition of BL did not result in substantial improvement of the oxidative stability of BL-PMEs. The oxidation stability which is defined by the induction period is the time elapsed between the start of the analysis and the time when the formation of oxidation products begins to increase rapidly. The results suggested that oxidation will occur faster in PME compared to BL and BL-PMEs. The oxidative stability of all BL-PMEs along with the neat BL and PME were within the acceptable limit according to ASTM D6751, EN 14214 and MS 2008.

It is suggested that the oxidation reactions of oils and fats involving the free radicals mechanism start with a dehydrogenation reaction to produce carbon-based free radicals (Wang *et al.*, 2020). Among the indicators used to evaluate the tendency of the dehydrogenation reaction to occur is the C-H bond dissociation energy, where a compound with lower bond dissociation energy is easier to oxidise, and thus possesses lower oxidative stability (Wang *et al.*, 2020). The C-H bond in PME is weaker compared to BL due to the presence of unsaturated fatty acids in PME. In addition, as described in the reaction kinetics of alkyl levulinates, due to the ketone carbonyl group and alkyl ester contributions, the bond dissociation energies around the carbonyl groups of alkyl levulinate are higher (Tian *et al.*, 2017). It is presumed that the absence of unsaturated components in BL makes it more stable than the unsaturated fatty acid chains in PME. Unlike antioxidants, it is presumable that the change of oxidative stability of BL-PMEs does not correspond to BL acting to prevent the auto-oxidation of oils like antioxidants. The oxidative stability of BL-PMEs is influenced by the oxidative stability property of BL itself as the number of BL increases in the blends.

A similar trend in the slight increase of oxidative stability for different biodiesel blends such as cottonseed oil biodiesel and dairy-washed milk-scum biodiesel has been reported on the use of oxygenated compounds; ethyl levulinate and ethyl acetoacetate, respectively, with both compounds possessing comparable oxidative stability >20 hr (Cao *et al.*, 2014; Joshi *et al.*, 2011). In contrast, a slight decrease in oxidative stability was reported in the addition of ethyl levulinate from 2.5% to 20.0% to poultry fat biodiesel, and the addition of ethyl levulinate and ethyl acetoacetate from 5.0% to 20.0% each to waste cooking oil biodiesel (Joshi *et al.*, 2011; Srikanth *et al.*, 2017). The different trends anticipated from the addition of oxygenated compounds on the oxidative stability of biodiesel blends are possibly related to the different unsaturation fatty acids present in these biodiesels. Further assessments are necessary to inspect the relationship between the unsaturation of fatty acid with different functional groups of the additives towards the oxidative stability of fuel blends.

Effects of BL on Calorific Value of BL-PME

Calorific value is the amount of heat released per unit quantity of fuel when burned completely and the products of combustion are cooled back to the temperature of the combustible mixture (Arbab *et al.*, 2013). A higher calorific value of a fuel is preferred since the heat release during combustion is facilitated (Arbab *et al.*, 2013). The calorific value of biodiesel is usually lower than that of diesel due to its oxygen content (Kaisan *et al.*, 2020; Wang *et al.*, 2017). The heating value is not specified in ASTM D6751 and EN 14214 but is prescribed in EN 14213 (biodiesel for heating purposes) with a minimum of 35 MJ kg^{-1} (Ali *et al.*, 2014). The calorific value of BL-PMEs was significantly different from PME ($p<0.001$). As the amount of BL increased from 5% to 15%, the calorific value of BL-PMEs decreased significantly to $p<0.001$ (*Table 4*). The calorific value of the BL-PME is within the requirement of EN 14213 for blending of BL up to 10%.

It was stated that the calorific value of fuel would be lower if the fuel had more oxygen content (Nanthagopal *et al.*, 2018). As alkyl levulinate is regarded as an oxygenated compound with oxygen content higher than that of diesel and biodiesel (Wang *et al.*, 2017), the decrease in calorific value of BL-PMEs is due to the increase in oxygen content of the fuel blends. A similar trend has been reported in previous studies on the addition of oxygenated compounds such as alcohols. This includes the addition of 1-butanol and 1-pentanol in *C. inophyllum* biodiesel (Nanthagopal *et al.*, 2018), pentanol in palm oil biodiesel (Radhakrishnan *et al.*, 2017), and ethyl levulinate and 1-butanol in diesel-biodiesels (Wang *et al.*, 2017). Since the addition of oxygenated compounds increases the oxygen content of the resultant fuels, a reduction in NOx and smoke emissions were observed (Nanthagopal *et al.*, 2018; Radhakrishnan *et al.*, 2017). Further study on the impact of BL on emission characteristics of BL-PME is necessary to truly assess its efficacy as a PME blend compound.

CONCLUSION

The effect of blending *n*-butyl levulinate (BL) at different amounts; 5%, 10% and 15%, with palm methyl ester (PME) on the fuel properties was evaluated. The BL-PMEs of all blending ranges satisfy the requirements of ASTM D6751 and EN 14214 for biodiesel in terms of acid value, flash point, and kinematic viscosity at 40°C. The cold flow characteristic of BL; low pour and cloud points, contributed to the enhancement of the BL-PME fuel properties. The addition of BL up to 15% has improved both cloud and pour points by 7°C. The high oxidative stability of BL increased the oxidative stability of BL-PMEs. Meanwhile, the calorific value of the BL-PME up to 10% BL is within the requirement of EN 14213, a minimum of 35 MJ kg^{-1}. The BL-PMEs properties were significantly different from PME ($p<0.05$). The properties were affected visibly ($p<0.05$) as the BL content increased. From the analysis, BL appears to be acceptable to be blended with biodiesel.

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